

DOUBLE LAYER STRUCTURES AND PATTERN FORMATION DURING SELECTIVE OXIDATION/REDUCTION OF GOLD SURFACES

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The development of an atomic/molecular-level and mechanistic understanding of structure and dynamic processes at electrified interfaces comprises one of the major goals in modern electrochemistry. Nanoscale structures on solid/liquid interfaces can be selectively created in an electrochemical environment by the potentiostatically controlled deposition and/or dissolution of material.

In model studies employing low index and stepped gold single crystals as well as thin, predominantly (111)-oriented gold films (20 nm) we performed structural and dynamic studies to explore pattern formation during controlled surface oxidation/reduction (ox/red) cycles/ steps. The mechanisms of these processes were monitored by electrochemical techniques, in-situ STM and SEIRAS (surface enhanced IR reflection/adsorption spectroscopy). Selective oxidation starts at sufficiently positive potentials at step edges, and subsequently, the reaction front grows onto terraces. Reversing the potential and completion of the surface oxide reduction allows to create defined nanoscale hole-patterns employing the tunneling tip as a “tool”. The average size and distribution of holes can be selectively controlled by application of a variable potential/time-regime of the red/ox-cycles. The electric field of the tip allows the selective dissolution of substrate material with high spatial resolution. As an example, the surface obtained after 10 ox/red cycles between 0.55V and 1.35 V (vs.SCE) **during** tunneling at the spot exhibits several atomic layers deep holes and channels. Positional change of 350 nm reveals significantly smaller features. An area which was only scanned **after** completion of 10 electrochemical ox/red cycles shows monotonically deep holes of close-to trigonal shape, which reflect nicely the symmetry elements of the Au(111)-surface. Only the latter represents “true” oxidation pattern of Au(111) in the absence of “tip-machining”. In-situ STM was employed to monitor (i) the relaxation of the created nanostructures and the (ii) functionalization of these hole- (“host”-) pattern by deposition of foreign metals and organic molecules. Comprehensive SEIRAS studies have been performed to follow chemical changes during and after completion of the ox/red cycles. Special attention is devoted to the evolution of the interfacial water structures as well as the role of anions during the surface transformations within the Helmholtz-region. Finally we will report on the dynamics of locally functionalized hole-(host)-guest patterns.

LITERATURE

D.Mayer, K.Ataka, Th.Wandlowski,J. Electroanal. Chem., in preparation

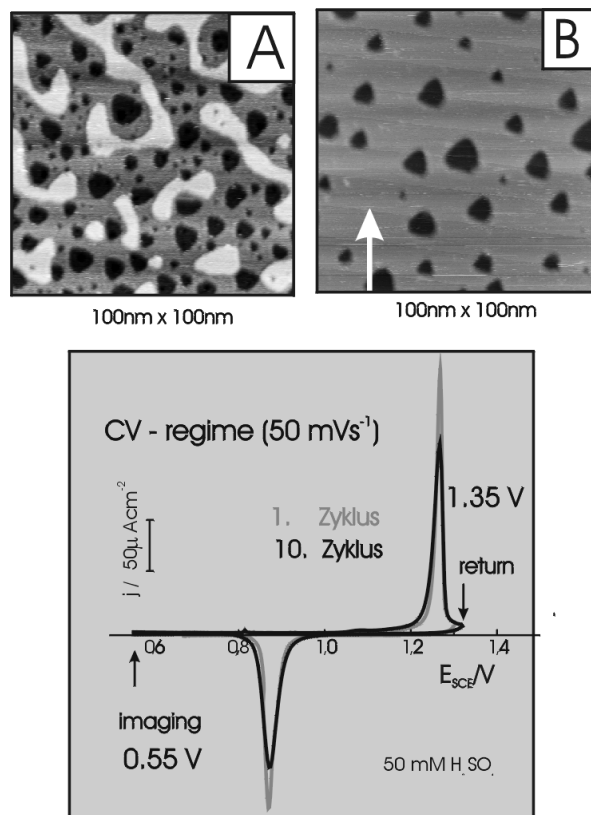


Abb.1: Au(111) in 0.05 M H₂SO₄ after 10 ox/red cycles between 0.55 V and 1.35 V (10 mVs-1) in the presence (A) and absence (B) of tunneling during ox/red.